JAN 26 1922

The Influence of Copper on the Rate of Solution of Iron in Acids.

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

FREDERICK KELLER BELL

BALTIMORE, MD.
June 1920

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ACKNOWLEDGMENT

THE author welcomes this opportunity to express his deepest sense of gratitude to Dr. Walter A. Patrick, at whose suggestion and under whose direction this investigation was carried out.

He also feels deeply indebted to Drs. Remsen, Frazer, Reid, Lovelace and Thornton for the inspiration received both in the lecture room and the laboratory.

The kind favors of Dr. S. W. Stratton, Director of the Bureau of Standards, as mentioned hereinafter specifically are sincerely appreciated.

THE INFLUENCE OF COPPER ON THE RATE OF SOLUTION OF IRON IN ACIDS.

Introduction.

The effect of the presence of small amounts of copper in iron on the corrosion of the latter is a subject on which there seems to be considerable debate. Buck[1] has found that a small copper content (0.2%) materially decreases the corrosion of steel sheets under atmospheric conditions. Aitchison[2] has shown from his corrosion experiments with 10% sulfuric acid that a 0.48% copper steel shows a greatly accelerated corrosion while 1.06%, 2.52% and 4.78% copper-steels show a marked decrease, the corrosion increasing slightly in the order given. Similar experiments carried out with the same alloys using tap water show, in general, an increased corrosion in comparison with pure carbon steel. Cushman[3] expresses the belief that "many earnest investigators have deceived themselves to the point of concluding that a little copper, say 0.25% or less, as an alloying constituent conferred resistivity on a steel." In this investigation we have restricted ourselves to the simplest case, *viz.*, the binary system of pure iron and pure copper; by determining the rate of solution in acids of such alloys (up to 5.0% copper) as well as that of pure iron, it was hoped that the true effect of the copper could be ascertained.

It was intended to study the rate of solution in hydrochloric and sulfuric acids of various concentrations. However, it was soon found that, in general, the rate of solution was too slow for the experimental method used; consequently, our experiments have been limited to more concentrated acids, *viz.*, 28.7% hydrochloric acid and 57.0% sulfuric acid.

Preparation of Materials.

The iron was prepared according to the method of Richards and Behr,[4] which is essentially the same as that used by Richards and Baxter[5] in their atomic weight determinations.

A good grade of piano wire was cleaned, cut up into convenient sized pieces, and dissolved in dilute nitric acid. Under these conditions, accord-

[1] Buck, *J. Ind. Eng. Chem.*, 5, 452 (1913).
[2] Aitchison, *Trans. Faraday Soc.*, 11, 212 (1916).
[3] Cushman, *ibid.*, 11, 242 (1916).
[4] Richards and Behr, *Z. phys. Chem.*, 58, 302 (1907).
[5] Richards and Baxter, *Z. anorg. Chem.*, 23, 245 (1900).

ing to Richards,[1] the silicon is precipitated either as silicic acid or as ferrosilicon (Fe_2Si) which is not attacked by dilute acid, and the carbon present as graphite and iron carbide is either completely oxidized or not attacked at all. By using dilute acid the possibility of oxidation of any sulfur to sulfate is diminished. The acid solution was filtered and concentrated by evaporation until crystallization took place on cooling. The ferric nitrate ($Fe(NO_3)_3.9H_2O$) thus obtained was recrystallized four times from dilute nitric acid solution to prevent hydrolysis and then in 200-gram lots, was heated in a platinum dish to 120° from six to eight hours, when the material was almost entirely dry; it was then removed and powdered, yielding a brilliant red powder. The conversion of the basic nitrate to the oxide was carried out at a red heat using a platinum resistance furnace described by Morse.[2] It was found that 30-grams basic nitrate heated in a platinum crucible for two hours at 900°, then repowdered and thoroughly mixed and finally heated again for one hour at 900° was completely converted to oxide. The oxide thus obtained was dark red and very finely divided.

Using a Hoskins electric furnace with a silica tube, 20 grams oxide was placed in a platinum boat and reduced in a current of commercial hydrogen at 600° for seven hours, and during the last hour at 1000°. The iron was obtained in silver-gray lumps, which could be powdered between the fingers. More than 300 grams of iron was prepared in this way the yields from the various reductions being thoroughly mixed together and stored in a glass-stoppered bottle.

The copper used was a sheet of pure copper foil which was first thoroughly cleaned with emery paper and then cut into small strips which were finally treated in the usual way, with methyl alcohol. The strips were cut into very small pieces and stored in a glass-stoppered container.

Preparation of the Alloys.

Five melts of 25 grams, each, containing 0.1%, 0.3%, 0.05%, 1.0% and 5.0% copper, respectively, were prepared and a pure iron melt of 40 grams. Through the kindness of Director Stratton the fusions were carried out at the Bureau of Standards laboratory in Washington.

Marquardt crucibles were used for the fusion. About half of the iron, *i. e.*, 12.5 grams, was weighed into the crucible and then a definite weight of copper added and finally more iron was added until the desired composition was obtained. In this way mixtures of the exact percentage composition listed above were prepared and fused in a vacuum electric

[1] Richards, *loc. cit.*
[2] Morse, *Am. Chem. J.*, *32*, 93 (1904).

furnace of the Arsem type.[1] The progress of the fusion was followed visibly through the mica window with which the furnace is equipped. After fusion the melts were retained in the molten condition until they became perfectly quiet, a period of from ten to fifteen minutes. The crucibles were removed from the furnace within an hour and a half after the heating element of the furnace had been cut off. A melt was also prepared from some of the Bureau of Standards electrolytic iron.[2] The melts thus obtained were with some difficulty due to their small size turned down on the lathe to uniform cylinders. In Table I the cross-sections of the cylinders are given.

TABLE I

DESIGNATION	% Cu.	CROSS SECTION. CM^2.
Melt 0 (Bureau of Standards pure electrolytic iron)	0.0	2.1408
Melt 1	0.1	2.1739
Melt 2	0.3	1.5890
Melt 3	0.5	1.9793
Melt 4	1.0	1.9320
Melt 5	5.0	1.5053
Melt 6 (Pure reduced iron)	0.0	2.2072

Description of Apparatus.

In devising the experimental method of measuring the rate of solution of the alloys we have frequently referred to and essentially adopted the method employed by Tzentnershyer,[3] who has worked extensively on the rate of solution of zinc and its alloys in acids by measuring the rate of evolution of hydrogen and we have sought to increase the accuracy of the method. The apparatus finally adopted may be best described by referring to the diagram in Fig. 1.

The thermostat T was of the type devised by Davis[4] and under the conditions of our experiments the temperature could be held constant within 0.02°. The reaction flask R, in which the acid and the alloy were placed, was equipped with a tightly fitting rubber stopper through which was introduced a gas-tight, mercury seal stirrer, S after the design of Reid[5] with the exception that it was equipped with only one exit tube and this led directly to a gas buret. The stirrer was geared directly to the shaft of the stirrer of the thermostat.

[1] Jour. Amer. Chem. Soc., 28, 921 (1906).
[2] Bur. Standards, *Bull.* 13, No. 1, 4 (1916).
[3] M. Tzentnershver and J. Drucker, *J. chm. phys.*, 13, 162 (1915); *J. Russ. Phys. Chem. Soc.*, 47, 1064 (1915); M. Tzentnershver and J. Sachs, Z. *physik. Chem.*, 89, 213 (1914); *ibid.*, 87, 692 (1914).
[4] P. B. Davis, *Carnegie Inst. Pub.*, 210, 121 (1915).
[5] E. E. Reid, Jour. Amer. Chem. Soc., 36, 2112 (1915).

The gas buret G, was of a special type compensating for both pressure and temperature. By means of the 3-way stopcock at W, the reaction flask, the manometer M and the gas buret proper could all be connected simultaneously and, of course, it was possible to connect any two of these units at the exclusion of the third one. The buret proper consisted of two arms. The right-hand arm was a 10-cc. pipet graduated in 0.05-cc. divisions and was sealed directly into the system. The left-hand arm was a specially blown glass tube consisting of four bulbs, each having a capacity of approximately 10 cc. but not greater than 10 cc. with reference to scratch marks which were placed on the constricted sections of the tube. The capacities of the bulbs were determined at 20° from the mercury capacity since the gas volumes were to be measured over mercury and were found to be (I) 9.616, (II) 9.235, (III) 8.965, and (IV) 9.627 cc. Since the accuracy of our measurements was to 0.01 cc. the capacities actually employed were 9.62, 9.24, 8.97 and 9.63 cc., respectively.

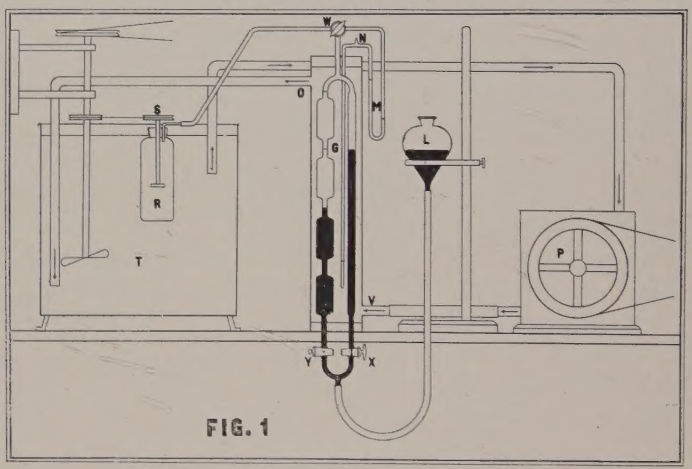


FIG. 1

The two arms of the gas buret were enclosed in a water jacket consisting of a glass cylinder with an inlet tube and an outlet tube sealed into its side below and above, respectively. The ends of the cylinder were closed by means of rubber stoppers through which the buret tubes were passed. Water was pumped (see Fig. 1) from the thermostat into the lower part of the water jacket through Tube V and thence out of the water jacket through Tube O which emptied into the thermostat. By regulating the velocity of the pump the temperature of the water in the water jacket never differed by more than 0.02° from that of the water in the thermostat.

Before the manometer M was sealed at N, a little water was introduced into the closed end of the manometer which was enclosed in the

water jacket so that the vapor pressure of the water would partially correct for the vapor pressure of the acid used and the manometer liquid, bromoform, was introduced into the U-shaped portion of the tube which was equipped with a millimeter scale.

Procedure.

Before each experiment the bulb tube of the buret was filled with mercury up to the top-most scratch mark and the stopcock Y was turned off. By adjusting the leveling bulb L the pipet tube was filled with mercury up to its zero reading, the stopcock X remaining open. A reading was then made of the barometric pressure, the system being under atmospheric pressure, and simultaneously a reading was made of the pressure difference as shown by the manometer M, and this reading was taken as the standard setting for a given experiment, *i. e.*, all volume readings were made with the pressure difference in the manometer equal to the standard setting which was accomplished by adjusting the leveling bulb.

Knowing the atmospheric pressure and the corresponding manometer pressure difference, the buret is then ready to be connected with the reaction flask. As the hydrogen is evolved the mercury in the pipet tube is displaced, the stopcock X being open while the stopcock Y is closed; and a corresponding alteration in the pressure difference in the manometer results. The leveling bulb was continually lowered so that the pressure difference in the manometer was practically always equal to the standard setting. When it was desired to read the volume the stopcock W was turned so that only the gas buret and the manometer were connected. The leveling bulb was then accurately adjusted until the manometer reading was identical with the standard setting and the volume read. This operation was easily completed within one minute after which the stopcock W was immediately turned to its original position. When the pipet tube was filled with hydrogen the gas was transferred to Bulb I in the bulb tube. This was accomplished by setting the stopcock W so that only the reaction flask and the manometer were connected. The stopcock Y was opened and by means of the leveling bulb the mercury level was brought to the lower scratch mark of Bulb I when stopcock Y is turned off. The leveling bulb was again adjusted so that the pipet is nearly filled with mercury. The stopcock W was then turned to its original position and the manometer reading was quickly adjusted to approximately the standard setting. In an exactly similar manner Bulbs II, III and IV could be filled consecutively.

We were thus able to measure gas volumes up to 50 cc. with an accuracy of 0.01 cc. at constant temperature and at constant pressure

which was practically atmospheric pressure thus minimizing the possibility of leaks in the apparatus. All experiments were carried out at 20° and the usual corrections were applied to the reading of the barometer. In the reduction of gas volumes to 0° and 760 mm. therefore, a constant factor could be employed.

Experimental.

It was, of course, necessary that a known surface of the alloys be exposed to the effect of the acid and to this end the cross-section of the cylindrical melts was taken as most suitable. Before each experiment the selected cross-section was first polished down with emery cloth (No. 00) after which it was finally polished on chamois using a fine grade of alumina as an abrasive. On the surface thus obtained there were some visible scratches but the main point was to obtain identical surfaces for all experiments.

The remaining surface of each cylinder, after cleaning in acid, was coated with a high-melting paraffin. Bakelite was tried for this purpose but was found to chip off readily. Experiments were first tried placing the alloy on the bottom of the reaction flask in a vertical position just beneath the stirrer, but the rate of evolution was not, in general, as uniform as when the alloy was fastened to the stirrer. This was accomplished by means of insulated copper wire which was wrapped around the alloys already protected with paraffin, and then around the stirrer, after which the wire was thoroughly coated with paraffin. Even under these conditions there was a strong tendency for the evolved hydrogen to form in bubbles on the paraffin to which they adhered tenaciously, and doubtless affected the observed uniformity of the hydrogen evolution, especially when the evolution was rapid. All experiments were carried out at a constant rate of stirring, and in all cases 200 cc. of acid was used.

The stopper of the reaction flask through which the stirrer was introduced and the melt attached to the stirrer could be handled as a single piece of apparatus. In starting an experiment the acid which had previously been suspended in a bottle in the thermostat was poured into the reaction flask and the stopper (with stirrer and melt attached thereto) was tightly inserted into the mouth of the reaction flask and the flask then clamped in its proper place in the thermostat. The exit tube of the reaction flask was connected then by means of rubber tubing with the glass tube leading to the gas buret. Finally the pulley of the stirrer was connected with a corresponding pulley on the shaft of the thermostat stirrer. Not more than one minute elapsed between the time the alloy first touched the acid and the time the flask was connected with the gas buret. The volume of the gas evolved was measured at definite time

intervals which, depending upon the magnitude of the volume change, varied from five minutes to one hour.

At the end of each experiment the metal cylinder was removed from the stirrer, thoroughly washed in water and dried. The surface which was exposed to the effect of the acid was examined under the microscope and micro-photographs and photographic enlargements of the total surface were made in order that any plating of copper might be detected.

Tabulation of the Experimental Data.

The data obtained from each experiment were tabulated under two columns. In the first column, under t, the time is given in minutes which has elapsed since the beginning of the experiment and the time the volume reading was made. The figures in the second column under $\frac{\Delta Vo}{\Delta t}$ /cm². are obtained by reducing to 0° and 760 mm. pressure the volume of hydrogen evolved between two consecutive volume readings divided by the time in minutes which has elapsed between the two readings and finally divided by the area of the surface of the metal in sq. cm. exposed to the action of the acid (see Table I), *i. e.*, the number of cc. of hydrogen at 0° and 760 mm. pressure evolved per minute per sq. cm. of surface.

The results of each experiment may be represented graphically by plotting the figures in Col. 1 against the corresponding values in Col. 2, *i. e.*, velocity-time curves.

Since the rates of solution are comparatively so small it should be noted that it has been necessary to exaggerate greatly the units of the vertical axis, *i. e.*, velocity, for purposes of reproduction in publication. When the various curves are plotted on a more appropriate scale such as unit velocity equivalent to 50 min., as employed by Tzentnershver,[1] the locus of the points is very closely represented by a smooth curve. This is especially true with the copper alloys, but in other experiments where the velocities are comparatively much higher the uniformity is less marked.

Experiments with Hydrochloric Acid.

For the experiments in hydrochloric acid a 28.0% acid was used, and was prepared by diluting concentrated C. P. acid with distilled water, the strength of the acid being determined by specific gravity measurements. Just before each experiment the metal cylinder to be used, already well protected with paraffin as has been previously described, was treated in a beaker with the 28% hydrochloric acid for 15 minutes, after which

[1] *Loc. cit.*

TABLE II

28% HCl at 20°

Expt. 1 Melt No. 6 0.0% Cu.		Expt. 2 Melt No. 6 0.0% Cu.		Expt. 4 Melt No. 1 0.1% Cu.		Expt. 5 Melt No. 2 0.3% Cu.		Expt. 6 Melt No. 3 0.5% Cu.		Expt. 7 Melt No. 4 1.0% Cu.		Expt. 8 Melt No. 5 5.0% Cu.		Expt. 9 Melt No. 0 0.0% Cu.	
t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²
0		0		0		0		0		0		0		0	
4	0.141	7	0.159	8	0.032	20	0.016	12	0.048	12	0.011	53	0.004	7	0.024
9	0.205	12	0.262	18	0.140	30	0.012	24	0.058	27	0.027	63	0.016	17	0.052
14	0.247	17	0.243	28	0.095	42	0.071	33	0.062	37	0.029	93	0.005	27	0.064
19	0.243	22	0.265	38	0.086	50	0.068	42	0.058	47	0.036	113	0.010	37	0.070
24	0.226	27	0.263	48	0.100	60	0.081	52	0.063	57	0.037	133	0.016	47	0.088
29	0.240	32	0.271	58	0.107	70	0.081	62	0.064	67	0.032	153	0.016	58	0.102
34	0.237	37	0.245	68	0.103	81	0.080	72	0.064	77	0.037	213	0.018	67	0.110
39	0.249	42	0.260	78	0.108	90	0.071	82	0.053	87	0.042	233	0.007	77	0.109
44	0.253	47	0.272	88	0.107	100	0.085	92	0.052	97	0.036	253	0.019	87	0.117
49	0.259	52	0.287	98	0.108	110	0.080	102	0.058	107	0.035	273	0.012	97	0.125
54	0.276	57	0.271	108	0.114	120	0.084	112	0.060	117	0.039	293	0.013	107	0.129
59	0.246	62	0.271	118	0.111	130	0.081	122	0.047	127	0.036	313	0.013	117	0.139
64	0.220	67	0.282	128	0.114	140	0.081	132	0.058	137	0.038	333	0.021	127	0.144
69	0.245	72	0.262	138	0.117	150	0.083	142	0.061	147	0.043	353	0.010	137	0.145
74	0.243	77	0.293	148	0.115	160	0.095	152	0.060	157	0.040	373	0.015	147	0.163
79	0.254			158	0.122	170	0.053	162	0.055	167	0.041	403	0.012	157	0.170
84	0.252			168	0.117	180	0.080	172	0.058	177	0.036	423	0.012	167	0.158
				179	0.100	190	0.085	182	0.059	187	0.037	443	0.015	177	0.174
				186	0.113	200	0.078	192	0.066	197	0.043	463	0.012		
						210	0.082	207	0.061	207	0.035				
						220	0.082	217	0.054						
Mean	0.246	Mean	0.268	Mean	0.110	Mean	0.079	Mean	0.058	Mean	0.037	Mean	0.013		

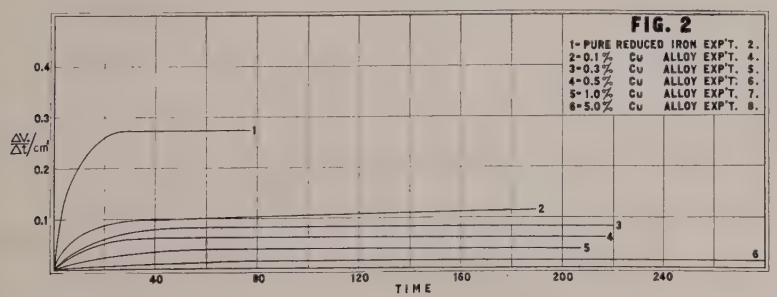
the experiment was started. In this manner it was expected that all it was removed and placed in the reaction vessel containing the acid and induction phenomena could be eliminated. This expectation was fulfilled, in general, and in most cases, due to the fact that the large excess of acid (200 cc.) remained practically constant in concentration during the comparatively short period of each experiment, the velocity of solution reached a constant maximum value shortly after the experiment was started. In such cases a mean of these maximum values has been taken and this value was considered as the rate of solution of metal under the experimental conditions.

The results of typical experiments are given in Table II under Expts. 1, 2, 4, 5, 6, 7, 8 and 9. In each case, with the exception of the Bureau of Standard's electrolytic iron (Expt. 9) the velocity reaches a maximum constant value the mean value of which has been taken, omitting in most cases the first value or two of the velocity. These means, with their average variations, are given in Table III. Experiments 2, 4, 5, 6, 7 and

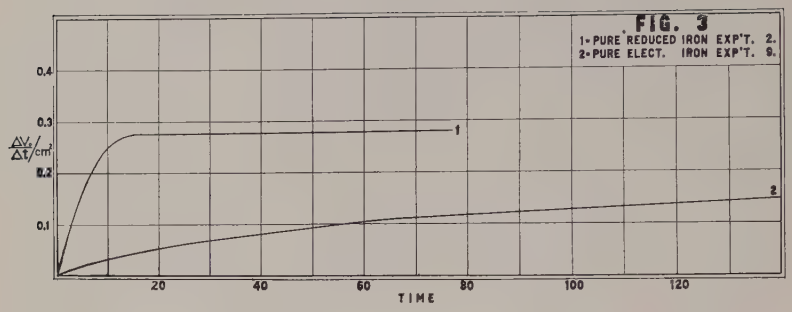
TABLE III.

Expt.	% Cu.	$\frac{\Delta Vo}{\Delta t}$/cm²		
1, 2	0.0	0.257	±	0.010
4	0.1	0.110	±	0.008
5	0.3	0.078	±	0.006
6	0.5	0.058	±	0.003
7	1.0	0.037	±	0.004
8	5.0	0.013	±	0.003

8 are shown graphically in Fig. 2, where the velocity has been plotted against the time. The Bureau of Standards' electrolytic iron shows a

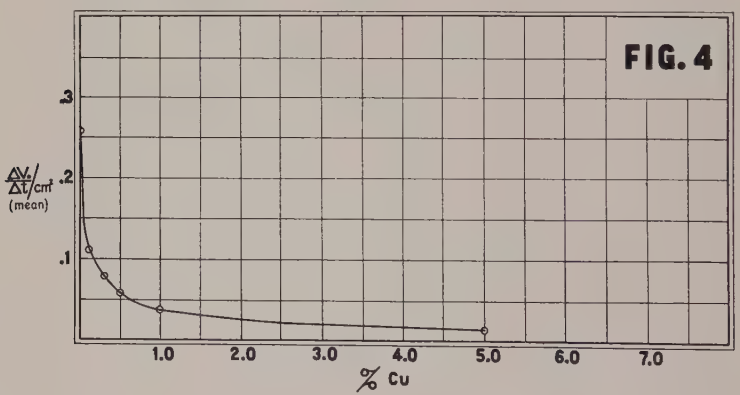


gradual increase in velocity and its relation to the behavior of the reduced iron is shown in Fig. 3, where the velocity-time curves of Expts. 2 and 9 have been plotted. In Fig. 4 the mean velocity of solution taken from Expts. 1, 2, 4, 5, 6, 7 and 8 has been plotted against the percentage of



copper giving the relation between the copper content and the rate of solution in 28% hydrochloric acid. For the value of the pure reduced iron we have taken 0.257, the average of the mean values of Expts. 1 and 2.

Several experiments were carried out in hydrochloric acid with the pure reduced iron (Melt 6) in contact with copper, silver and platinum. This was accomplished in the following manner. A piece of wire of the desired metal, thoroughly cleaned, was tightly wrapped once around the metal cylinder which had not yet been coated with paraffin so that the top-most portions of the wire were flush with the surface, already pol-



ished, which was to be subjected to the action of the acid (see Plate V). The bottom and the sides of the metal cylinder were then covered with paraffin as far as the under side of the wire so that the greater portion of the surface of the wire would be in contact with the acid as well as that of the iron. The rest of the procedure was identical with that of the

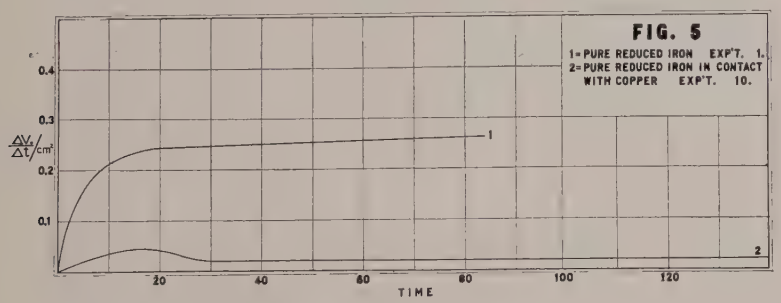
TABLE IV

28% HCl at 20°

Pure Reduced Iron (Melt No. 6) in contact with:

Copper Expt. 10		Platinum Expt. 11		Platinum Expt. 12		Silver Expt. 13		Silver Expt. 14	
t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²	t	$\frac{\Delta Vo}{\Delta t}$ —/cm²
0		0		0		0		0	
5	0.070	5	0.162	5	0.220	5	0.139	5	0.224
10	0.035	10	0.242	10	0.278	10	0.253	10	0.248
15	0.044	15	0.266	15	0.294	15	0.254	15	0.254
25	0.029	20	0.261	20	0.303	20	0.261	20	0.269
35	0.019	25	0.271	25	0.283	26	0.268	25	0.271
45	0.018	30	0.260	30	0.285	30	0.273	30	0.288
55	0.026	35	0.285	35	0.283	35	0.275	35	0.284
65	0.013	40	0.283	40	0.289	40	0.274	40	0.298
75	0.021	45	0.281	45	0.295	45	0.279	45	0.297
85	0.019	51	0.265	50	0.275	50	0.298	50	0.303
95	0.021	55	0.291	55	0.275	55	0.282	55	0.297
105	0.026	59	0.296	60	0.295	60	0.296	60	0.311
115	0.020	65	0.285	65	0.260	65	0.294	65	0.311
130	0.016	60	0.291	70	0.257	70	0.301	70	0.303
140	0.019	74	0.283			74	0.304		
Mean	0.020	Mean	0.278	Mean	0.283	Mean	0.280	Mean	0.287

previous experiments. The results of these experiments are tabulated in Table IV. The corresponding velocity-time curves are given in Figs. 5 to 9. The average velocity of solution in the experiment with the copper wire (Expt. 10) corresponds to an approximately 2.0% copper alloy according to Fig. 4. A qualitative experiment was also carried out with the iron in contact with copper. The two metals in contact were placed

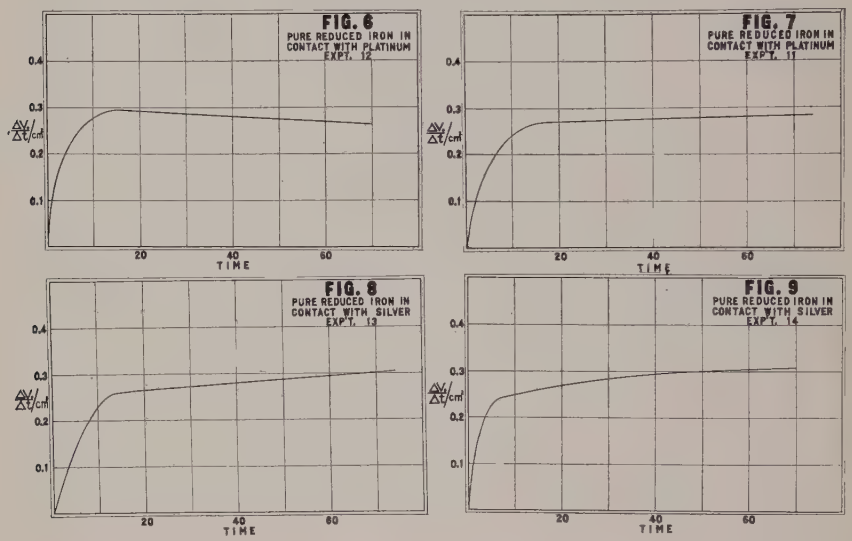


in an open beaker containing 28% hydrochloric acid. No evolution of hydrogen from the copper could be detected.

The average velocities obtained in the platinum and silver experiments are slightly higher than those of the pure iron; however, there is a small but significant increase in surface, consisting of a narrow band around the side of the cylinder extending, in width, from the top surface of the melt to the point where the wire is in contact with the iron. If

correction could be accurately made for this surface the velocities would probably check closely with those of pure iron.

Microscopic examination of the surface exposed to the action of the acid showed in no case the presence of copper plating. The surfaces when thoroughly cleaned retained their brilliant metallic luster for some time. Microphotographs (see Plate I) and enlarged (app. 8 times) photographs (see Plates II, III, IV and V) showing the total surface exposed to the action of the acid, offer visible evidence of the fact that copper decreases the rate of solution of iron in concentrated hydrocloric acid. In the absence of copper or in the presence of platinum the iron is deeply



eroded between the crystals. On the other hand, in the case of the copper alloys or in the case of the copper band around the pure iron, a greatly diminished erosion is indicated by the photographs.

It was thought advisable to determine the agreement between the total hydrogen evolved and the iron content in the acid solution at the end of an experiment. For this purpose the solutions from Expts. 11, 12, 13 and 14 were analyzed. The following method of analysis was used. The solution strong in hydrochloric acid was evaporated with sulfuric acid until fumes of sulfur trioxide were evolved. The residue was diluted with water and then titrated with permanganate. The ferric iron thus obtained was titrated with titanium trichloride, using ammonium thiocyanate as an indicator. All of the results thus obtained were consistently higher than the corresponding hydrogen volume values. An explanation

PLATES

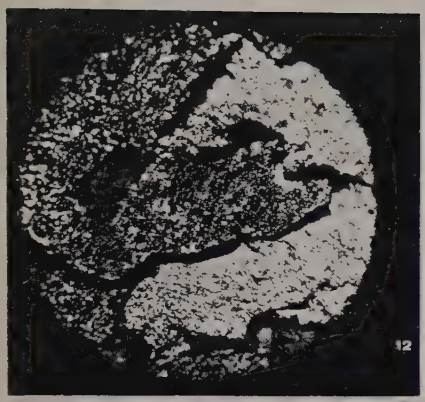
I ∴ to ∴ V

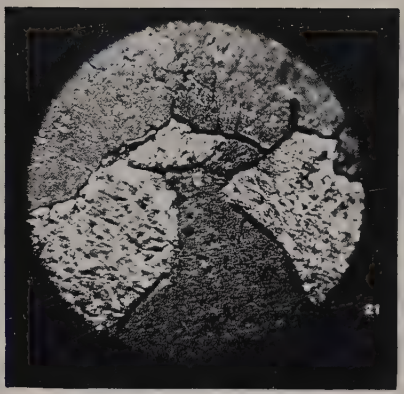
INCLUSIVE

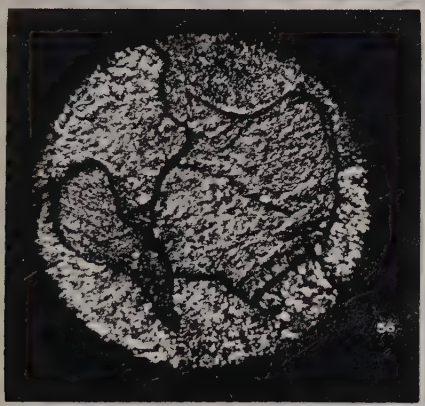
PLATE I.

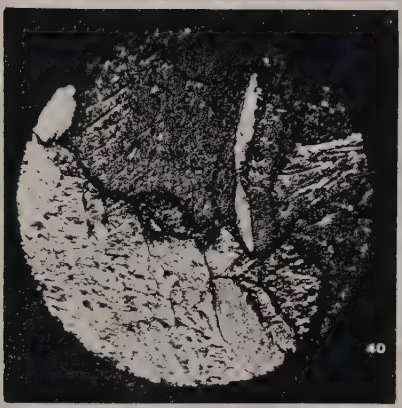
Microphotographs (50 times).

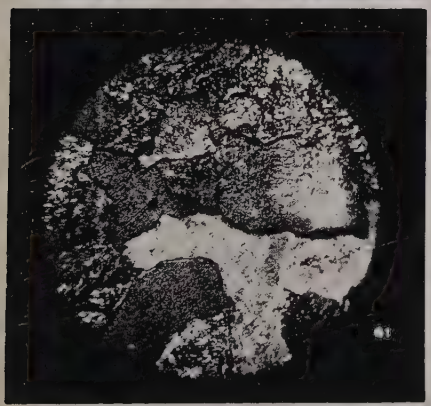
12—Pure reduced iron, after Experiment 1.
21—0.1% copper alloy, after Experiment 4.
56—0.3% copper alloy, after Experiment 5.
40—0.5% copper alloy, after Experiment 6.
61—1.0% copper alloy, after Experiment 7.
82—5.0% copper alloy, after Experiment 8.


12


21


56


40


61

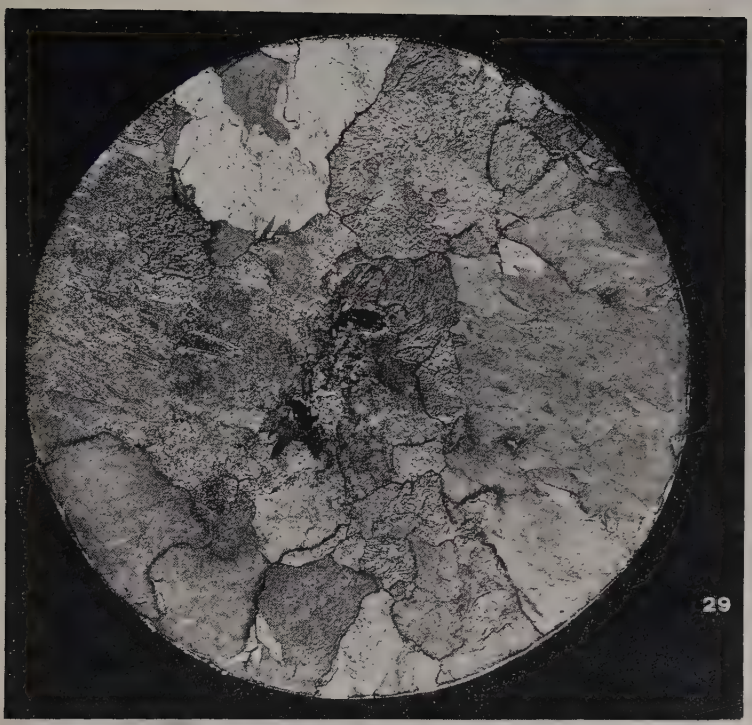
82

PLATE II.

Enlarged (8 times) photographs of total surface.

29—0.1% copper alloy, after Experiment 4.

15—Pure reduced iron, after Experiment 1.


29

15

PLATE III.

Enlarged (8 times) photographs of total surface.

54—0.3% copper alloy, after Experiment 5.
46—0.5% copper alloy, after Experiment 6.

54

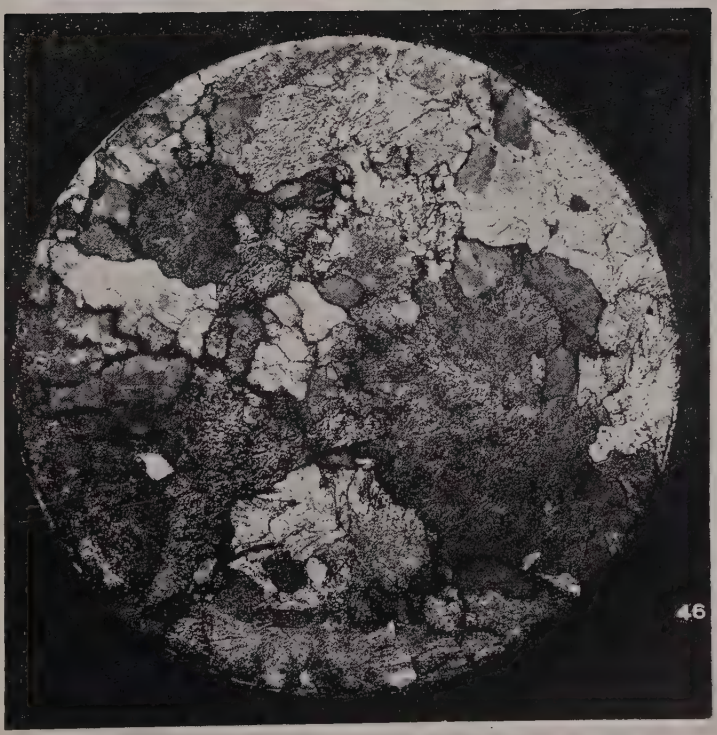
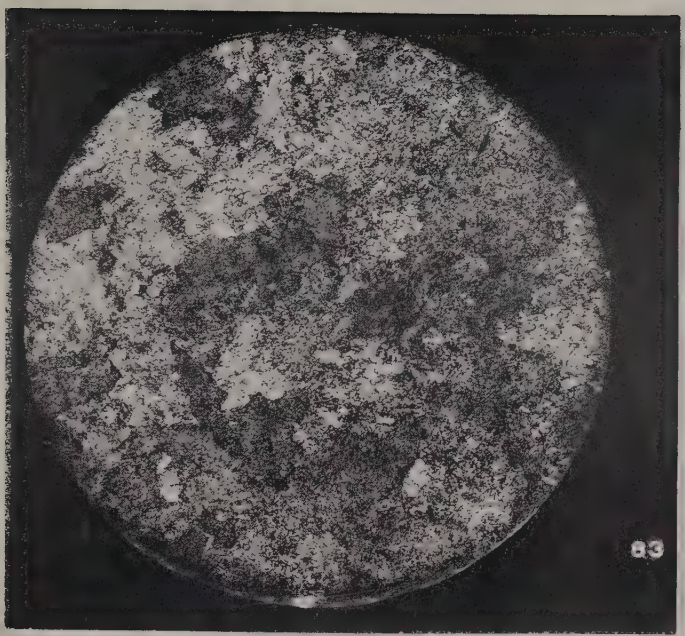

46

PLATE IV.

Enlarged (8 times) photographs of total surface.

83—5.0% copper alloy, after Experiment 8.
63—1.0% copper alloy, after Experiment 7.


83

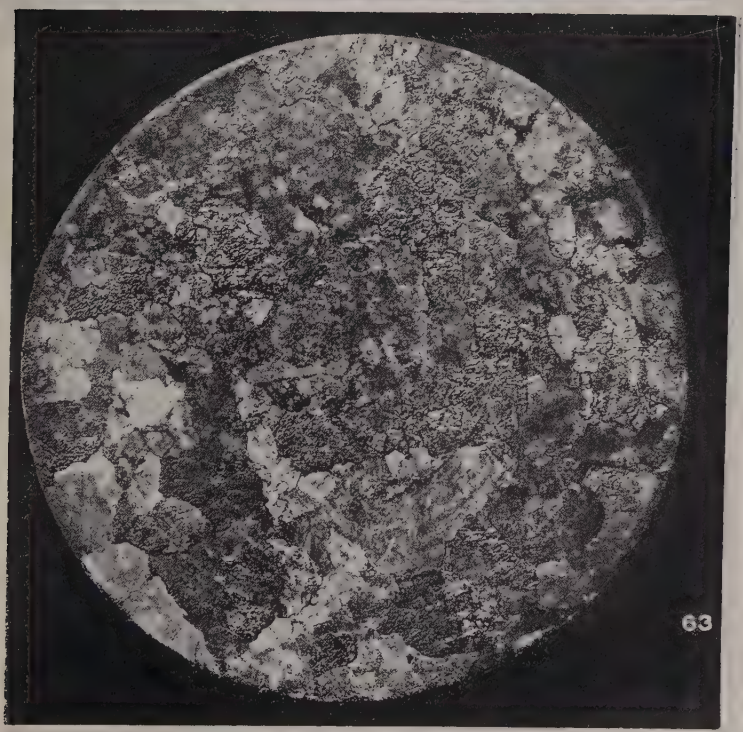
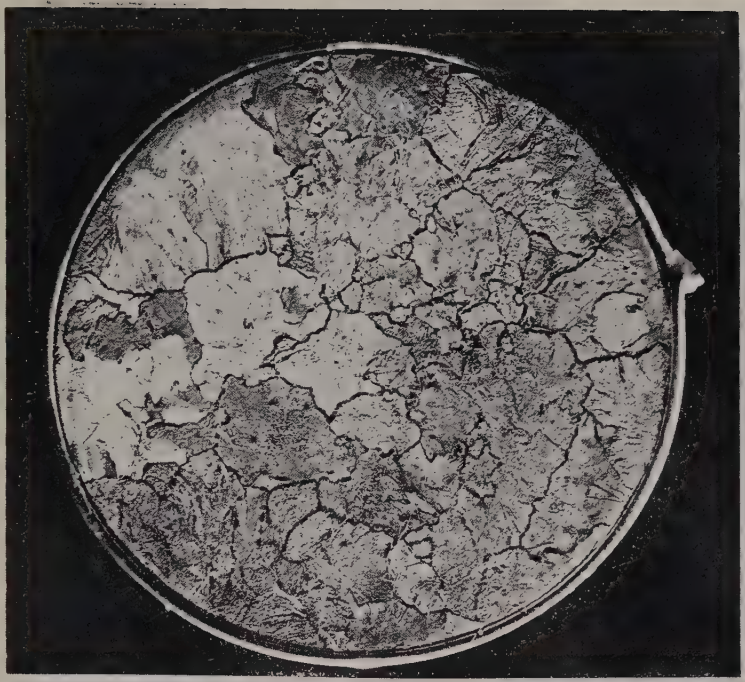
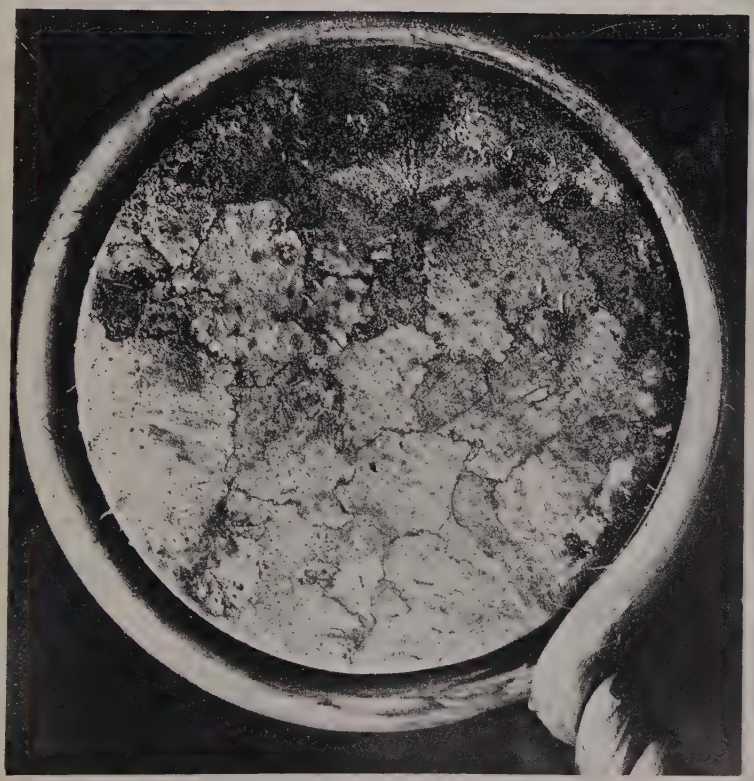

63

PLATE V.

Enlarged (8 times) photographs of total surface.

Pure reduced iron in contact with:
Bottom—Copper, after Experiment 10.
Top—Platinum, after Experiment 11.



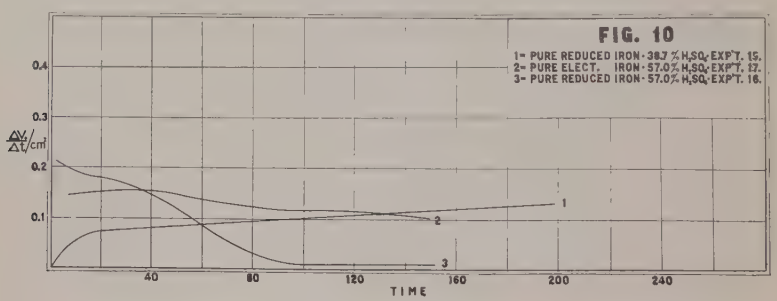


of this difference may be based on the following considerations. (1) The solubility of hydrogen in the acid solution; (2) the occlusion of hydrogen by the metal; and (3) the adherence of gas (hydrogen) bubbles to the walls of the reaction chamber and to the paraffin coating of the metal, which was always apparent and perhaps the most significant factor.

Experiments with Sulfuric Acid.

The acids used in these experiments were prepared by diluting concentrated c. p. acid with distilled water. The composition was determined from the specific gravity.

Using the pure reduced iron (Melt 6) an experiment was made in 38.7% acid after a preliminary treatment of 15 minutes in acid of the same strength. The results of this experiment are shown graphically in Fig. 10, tabulated under Expt. 15. The rate of solution showed a steady increase with the time. In the hope of obtaining a rate of solution comparable to the corresponding experiment in hydrochloric acid the concentration of the acid was increased to 57% and the preliminary treatment consisted of five minutes in contact with concentrated hydrochloric acid and then, after thorough washing, ten minutes in 57% sulfuric acid. The electrolytic iron was treated in the same way. The results of these experiments, 16 and 17, are shown graphically in Fig. 10.



The results obtained with the 57% acid were very unsatisfactory. In the case of Melts 1, 2 and 3 the solution was extremely slow, and after a period of about two hours a decrease in volume was observed. Expt. 18 is given as representative of several experiments in which the decrease in volume was noted. In these experiments the surface of the melt became covered with a dark smudge which, when analyzed on removal, gave a negative test for copper. At the end of one experiment it was thought that the odor of hydrogen sulfide was detected on emptying the gas buret. Several attempts to confirm this observation gave negative results.

With Melts 5 and 6 (Expts. 19 and 20, respectively) the rate of solu-

tion was very slow but no volume decrease was observed. In Expt. 20 (5.0% copper) there was a visible plating of copper on the metallic surface within 5 minutes after the experiment was started.

On removal from the acid after an experiment all the melts showed a strong tendency to oxidize even after thorough cleaning and drying. The surfaces were immediately examined under the microscope. Microphotographs and enlarged photographs of the total surface exposed to the acid were prepared. In the entire investigation a copper plating was detected only after Expt. 20 and in this case the plating was plainly visible to the naked eye.

Discussion of Results.

It cannot be too strongly emphasized that the acids employed in the present investigation were concentrated. The reasons for confining ourselves to such strength of acids were found in the fact that our method of following the rate required the use of strong acids in order to obtain an appreciable gas evolution. This fact is mentioned in order that our results will not be extrapolated to include weak acids and conclusions drawn as to the ordinary corrosion of copper-iron alloys. We do not know what would take place in weak acids.

Theories have been advanced to explain the retarding action of copper upon the rate of solution of iron in acids. In the present discussion no serious attempt will be made to explain the phenomenon, inasmuch as at the present time we have not collected our complete experimental data. Nevertheless, our experiments are sufficient to disprove several of the explanations which have been advanced.

We can dismiss at once the question of the influence of the copper upon the usual impurities occurring in ordinary iron or steel, inasmuch as our iron was pure. Similarly, the influence of copper upon the grain size is clearly without effect.

Likewise, the question of the electrode potential of an iron-copper alloy is of no weight because we observe the same retarding effect with metallic copper in contact with pure iron (see Expt. 10). In this connection it should be mentioned that up to 8.0% copper, iron-copper alloys have been found to exist as solid solutions,[1] and recent work by Tammann[2] indicates that the electrode potential of most alloys which exist as solid solutions does not vary continuously with the composition.

[1] Stead, *J. Iron Steel Inst.*, 11, 112 (1901).
[2] Tammann, *Z.anorg. Chem.*, 107, 136 (1919); 109, 80 (1919).

Another explanation that has been offered is that the decreased rate of solution is due to a deposit of metallic copper over the surface of the iron. Our microscopic sections do not reveal any trace of copper. The 5.0% copper alloy in sulfuric acid showed a marked deposit of copper, but in no case did this occur in the experiments with hydrochloric acid.

It has been suggested by Tzentnershver[1] that passivity of the metal is produced by the alloyed metal and that this is the explanation of the retarded solution rate. At first sight this idea appears rather attractive but is not able to stand against the experimental facts. In sulfuric acid we found that our 5.0% copper alloy became coated with copper (Expt. 20), notwithstanding the fact that passive iron does not precipitate copper from solution. Furthermore, it is well known that the chloride ion is most effective in preventing iron from becoming passive, nevertheless our experiments in hydrochloride acid showed a marked retardation in the rate of solution of the alloys.

The question of overvoltage has been mentioned in connection with the phenomenon. If it is more difficult for hydrogen to be evolved from the copper than it is from the iron, then copper in contact with the pure iron should not interfere with rate of solution and this is contrary to the results obtained in Expt. 10. Furthermore, the experiments with platinum in contact with iron are most conclusive on this point. It is to be remembered that platinum exerted practically no effect on the rate of solution of the iron. This is clearly a point against the overvoltage theory, inasmuch as platinum possesses such a low overvoltage. If the curve in Fig. 4 is examined it will be seen that the rate of solution decreases with increase in copper content and then gradually reaches a practically constant value. The form of the curve also shows that the rate of solution is not inversely proportional to the copper content. In fact, it appears that a considerable area of iron is affected by the presence of copper. One might say that the copper is surrounded by a sphere of influence within which hydrogen ions are discharged with difficulty. This idea is suggested by an examination of the action of acid upon iron in contact with a piece of copper. It is noticed that there is a visible diminution of the evolution of hydrogen throughout a zone in the vicinity of the copper.

The explanation of the retardation observed in hydrochloric acid that suggests itself after a study of the experimental evidence unfortunately is not proved and we therefore only offer it tentatively. It is this.

[1] *Loc. cit.*

Copper is dissolved in strong acids to a limited extent. This solution of copper is possible because of the formation of complexes[1] with the acid thereby reducing the copper ion concentration to such an extent that hydrogen ions may be electrically discharged. This dissolved copper, however, in the presence of iron does not remain in solution but is precipitated out in a finely divided state. This latter state of the copper renders it more readily attacked by the acid and it redissolves and we have the copper oscillating back and forth between the solution and the surface of the iron. The changes may be written thus:

$$Cu + 2H^{+} = Cu^{++} + H_2 \qquad (I)$$

$$Cu^{++} + Fe = Fe^{++} + Cu \qquad (II)$$

Reaction II undoubtedly occurs very rapidly and the occurrence of Reaction I is responsible for the retardation of the rate of solution of the iron, *i. e.*,

$$Fe + 2H^{+} = Fe^{++} + H_2. \qquad (III)$$

The initial amount of the copper dissolved which depends upon the copper content of the alloy for a given acid concentration is considered then as being intermittently precipitated in a finely divided state and, therefore, more soluble than the copper of the alloy and redissolved and this layer of precipitated copper which is intermittently present on the surface of the iron retards the solution of the latter, *i. e.*, Reaction III.

Summary.

1. The rates of solution of pure electrolytic iron and pure reduced iron and 0.1%, 0.3%, 0.5%, 1.0% and 5.0% copper alloys of the latter have been determined in 28.7% hydrochloric acid at 20°.

2. The rate of solution of the alloys shows a definite decrease in comparison with pure reduced iron as the copper content increases.

3. The rate of solution of pure reduced iron in contact with platinum, silver, and copper in 28.0% hydrochloric acid at 20° has been measured. Platinum and silver show apparently no effect while copper greatly lowers the velocity.

4. Experiments in 57.0% sulfuric were unsatisfactory lacking in uniformity and suggesting that experimental conditions were not under control.

5. An explanation of the retarding effect of copper in hydrochloric acid has been offered.

[1] Odling, *J. Chem. Soc.*, 9, 291 (1857); Berthelot, "Mecanique chemique," Vol. II, 524; Engel, *Compt. rend.*, 121, 528 (1895).

BIOGRAPHY.

FREDERICK KELLER BELL, the author of this dissertation, was born at Cincinnati, Ohio, on March 27, 1895. His early education was obtained in the public schools at Baltimore, Maryland, and culminated in his graduation from the Baltimore City College in June, 1912. He was graduated from the Johns Hopkins University with the degree of Bachelor of Arts in June, 1916. In the fall of the same year he entered the Graduate Department of Chemistry of the Johns Hopkins University. His subordinate subjects were Physical Chemistry and Mathematics. During the year 1916-17 he was laboratory assistant in collegiate chemistry under Drs. Gilpin and Miller. The period from May, 1918, to December, 1918, was spent in government service. He was awarded Hopkins Scholarships for the years 1917-18, 1918-19, and 1919-20.

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